

ARMY RESEARCH LABORATORY



Relative Solubility of RDX and TNT in Supercritical CO₂

by Jeffrey B. Morris

ARL-TR-1343

April 1997

19970703 084

Approved for public release; distribution is unlimited.

INFORMATION REPORTED 1

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer need. Do not return it to the originator.

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5066

ARL-TR-1343

April 1997

Relative Solubility of RDX and TNT in Supercritical CO₂

Jeffrey B. Morris

Weapons and Materials Research Directorate, ARL

Abstract

Mixtures of 2,4,6-trinitrotoluene (TNT) and the nitramines cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) are used in a variety of high-explosive formulations, such as Composition B (RDX/TNT) or Octol (HMX/TNT). There has been much recent interest in the use of supercritical fluid (SF) CO₂ technologies for the processing and/or demilitarization of energetic materials. The solubility of RDX in neat CO₂ was measured over a temperature and pressure range of 303–353 K (30°–80° C) and 6.9–48.3 MPa (1,000–7,000 lb/in²) and is presented in this report.

RDX was found to be relatively insoluble in neat CO₂ in the temperature and pressure range studied, with a maximum solubility of about 0.25mg/g of CO₂. Data for TNT solubility in CO₂ have recently been published by a group of researchers at the Fraunhofer Institut für Chemische Technologie. Consideration of the relative solubilities of RDX and TNT in CO₂ suggests that SF extraction (SFE) of TNT should be effective for separation and recovery of nitramine materials from TNT-based energetic formulations. RDX is found to be 2-3 orders of magnitude less soluble than TNT in SF CO₂. An SFE-based separation process is demonstrated on a synthetic mixture of RDX and TNT powders.

ACKNOWLEDGMENTS

This work was supported by the Strategic Environmental Research and Development Program, project PP-660.

INTENTIONALLY LEFT BLANK.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	iii
LIST OF FIGURES	vii
LIST OF TABLES	ix
1. INTRODUCTION	1
2. EXPERIMENTAL	2
3. RESULTS AND DISCUSSION	7
3.1 RDX Solubility in CO ₂	7
3.2 TNT Solubility in CO ₂	11
3.3 Comparison of RDX and TNT Solubilities in CO ₂	12
4. CONCLUSIONS	15
5. REFERENCES	17
DISTRIBUTION LIST	23
REPORT DOCUMENTATION PAGE	27

INTENTIONALLY LEFT BLANK.

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Representative single-component phase diagram	1
2. Apparatus for measurement of RDX solubility in supercritical CO ₂ . The drawing of the extraction unit shows the multiport valve and the extraction vessel that is filled with RDX	4
3. Apparatus for calibration of the UV-Vis detector	4
4. Spectral shift of RDX in CO ₂ relative to RDX in acetonitrile calibration solutions . . .	6
5. Typical RDX solubility profile in CO ₂ at 246 nm. The extraction vessel was put online at 10 min	6
6. Density of CO ₂ as a function of temperature and pressure	9
7. RDX mole fraction in CO ₂ as a function of temperature and pressure	10
8. Vapor pressures of RDX and TNT, plotted as log(P _{vap}) versus temperature	14
9. Separation of a mixture of RDX and TNT powders using CO ₂ at 323 K and 13.8 MPa: chromatograms using 246 nm detection of (A) unextracted mixture and (B) recovered material following extraction. The unidentified peak in (A) is due to the acetone used to dissolve the sample; acetonitrile was used to dissolve the recovered material in (B)	14

INTENTIONALLY LEFT BLANK.

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Solubility of RDX in CO ₂ (Milligrams RDX/Gram CO ₂) as a Function of Temperature and Pressure	8
2. RDX Vapor Pressure (P _{vap}) and Fitting Parameters for RDX Solubility in CO ₂	9
3. Solubility of TNT in CO ₂ (Milligrams TNT/Gram CO ₂) as a Function of Temperature and Pressure	11
4. Solubility Ratios of TNT Relative to RDX in CO ₂ as a Function of Temperature and Pressure.	12

INTENTIONALLY LEFT BLANK.

1. INTRODUCTION

The use of supercritical fluids (SFs) for the analysis, processing, or demilitarization of energetic materials and important related inert ingredients has been under investigation for about the last 10 years. These studies fall into the categories of extraction of propellant stabilizers and plasticizers [1–11], extraction and/or recrystallization of energetic fillers [1,12–18], and extraction of polymers and waxes [19–22]. SFs possess liquid-like densities, gas-like diffusivities and viscosities, and low surface tensions [23]. These properties make SFs attractive as processing solvents. However, as Chester, Pinkerton, and Raynie point out in their recent review article [24], any single-phase fluid, including liquids, may be suitable for carrying out extraction processes.

Figure 1 shows a representative single-component phase diagram. Phase transition equilibrium curves separate the regions of solid, liquid, and gas. Of particular interest is the liquid-gas equilibrium curve, which terminates abruptly at the critical point. The temperature and pressure at the critical point are defined as the critical temperature (T_c) and critical pressure (P_c). An SF results when the temperature and pressure are greater than these critical parameters.

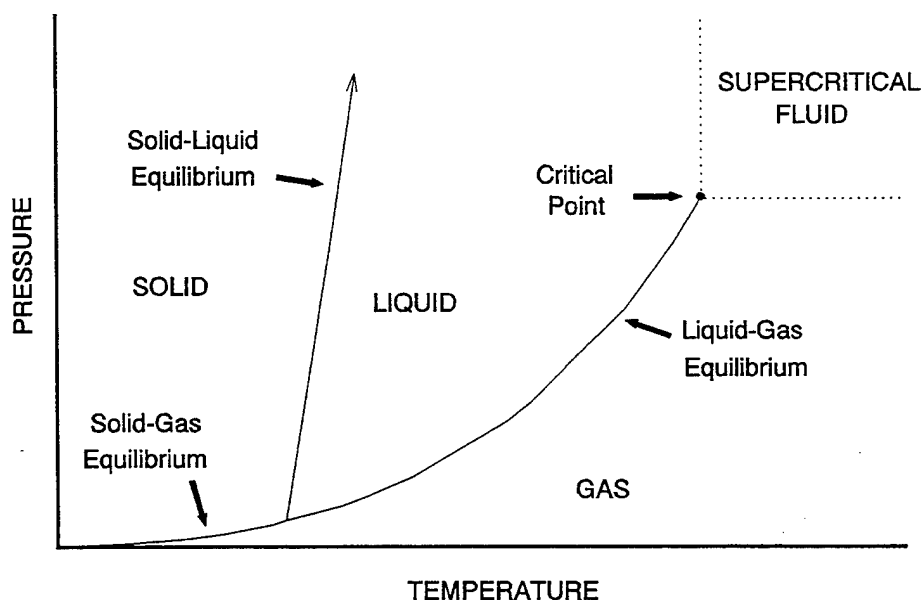


Figure 1. Representative single-component phase diagram.

One technology developed for demilitarization of energetic materials during the last decade is the U.S. Army Missile Research, Development, and Engineering Center (formerly U.S. Army Missile Command [MICOM]) liquid ammonia process for the recovery of ammonium perchlorate (AP), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX) from rocket propellant [25–29]. Results from work done at the U.S. Army Research Laboratory (ARL) indicate that it should also be possible to dissolve and recover RDX from a formulated energetic material by selecting an appropriate polar modifier for supercritical CO₂ [15–18]. However, direct extraction of RDX may not be the preferred route when one considers that RDX is often the primary ingredient in an energetic formulation. It may make more economic sense to extract the secondary ingredients, such as stabilizers, plasticizers, and certain binder ingredients. While mass transfer or diffusion limitations can have a large influence on an extraction process, it is clear that the solubilities of all the chemical components involved need to be considered for solvent selection and process design.

CO₂ is arguably the most environmentally benign solvent known, next to water. CO₂ is not an ozone-depleting substance. While CO₂ is a greenhouse gas, its production can involve a number of natural sources [30], so the capture and use of CO₂ can be thought of as a temporary diversion from its ultimate atmospheric fate. CO₂ is abundant and cheap at 3 cents per pound in bulk.

A large body of literature exists on the use of CO₂ as an extraction solvent [24,31]. The critical parameters for CO₂ are easily accessible, with $T_c = 304.2$ K and $P_c = 7.38$ MPa [30]. The solubility data for RDX in CO₂ are limited, with indications that RDX and HMX are both fairly insoluble in this solvent [1]. In contrast, an extensive set of solubility data for 2,4,6-trinitrotoluene (TNT) in CO₂ have recently been reported by a group at the Fraunhofer Institut für Chemische Technologie (ICT) [32]. As will be seen below, TNT is up to 3 orders of magnitude more soluble in CO₂ than is RDX.

2. EXPERIMENTAL

The equipment used to determine the solubility of RDX in supercritical CO₂ is shown in Figure 2. A 260-ml syringe pump (ISCO model 260 D) was filled with neat liquid CO₂. One of the multiport

valves on a small supercritical fluid extraction (SFE) unit (CCS Instrument Systems) was configured to bring a 1-ml extraction vessel online or offline of the CO₂ flow. The extraction vessel was filled with RDX, and the RDX particle size was kept below 150 µm in order to maximize the ratio of surface area to mass, which helps to ensure rapid saturation of the fluid with the solute. A liquid chromatographic multiwavelength ultraviolet-visible (UV-Vis) detector (Thermo Separation Products), equipped with internal light sources and a high-pressure flow cell, was used to detect RDX levels in the fluid. The detector wavelength was set to 246 nm for the solubility measurements. The flow cell and the transfer line from the extraction unit were thermally stabilized using a water circulator. A variable linear restrictor (ISCO) was used to adjust the CO₂ flow rate through the system. As the CO₂ exited the flow restrictor, its pressure dropped to ambient. The resulting gas was bubbled through acetonitrile in a collection flask, where the RDX that was initially dissolved in the CO₂ would be trapped.

The experimental setup was modified for detector calibration, as shown in Figure 3. A transfer line with a 2-ml sample injection loop was connected between the syringe pump and the flow cell on the UV-Vis detector, and the variable restrictor was removed. The detector was put into scan mode over a range of 200–400 nm with 1-nm resolution. The syringe pump was filled with acetonitrile and was set to a constant flow rate of 0.5 ml/min.

The sample injection loop was filled with calibration standards of RDX in acetonitrile. The sample loop was brought online, and spectra of each calibration standard were recorded. Spectra from the three most dilute calibration standards (20–80 mg RDX/l acetonitrile) were averaged. The original experimental setup was restored, and seven spectra of RDX in supercritical CO₂ were taken over a range of 308–353 K and 20–40 MPa. These spectra were examined for variations in the RDX

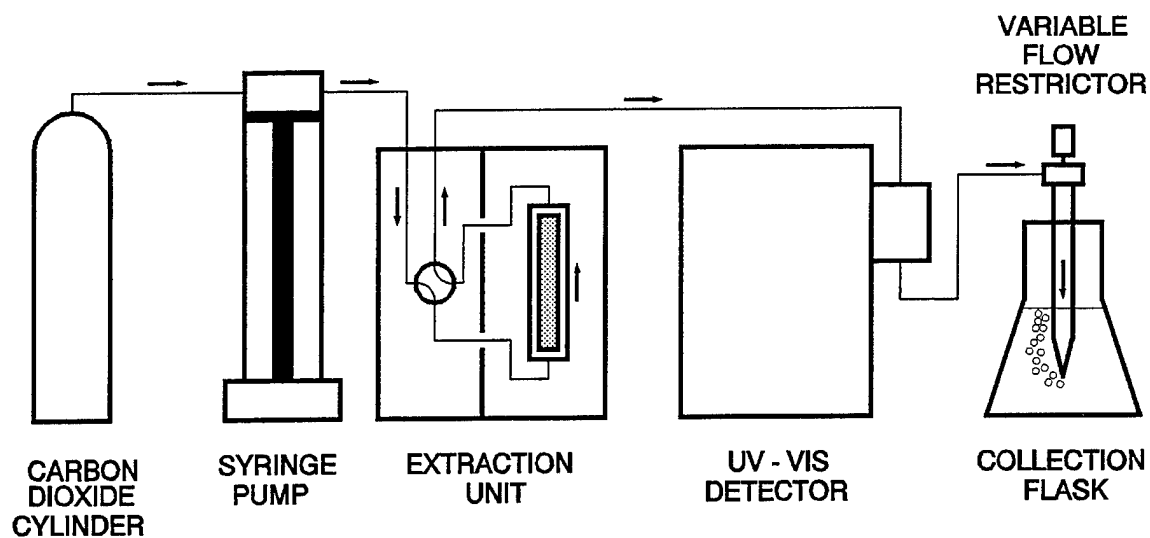


Figure 2. Apparatus for measurement of RDX solubility in supercritical CO₂. The drawing of the extraction unit shows the multiport valve and the extraction vessel that is filled with RDX.

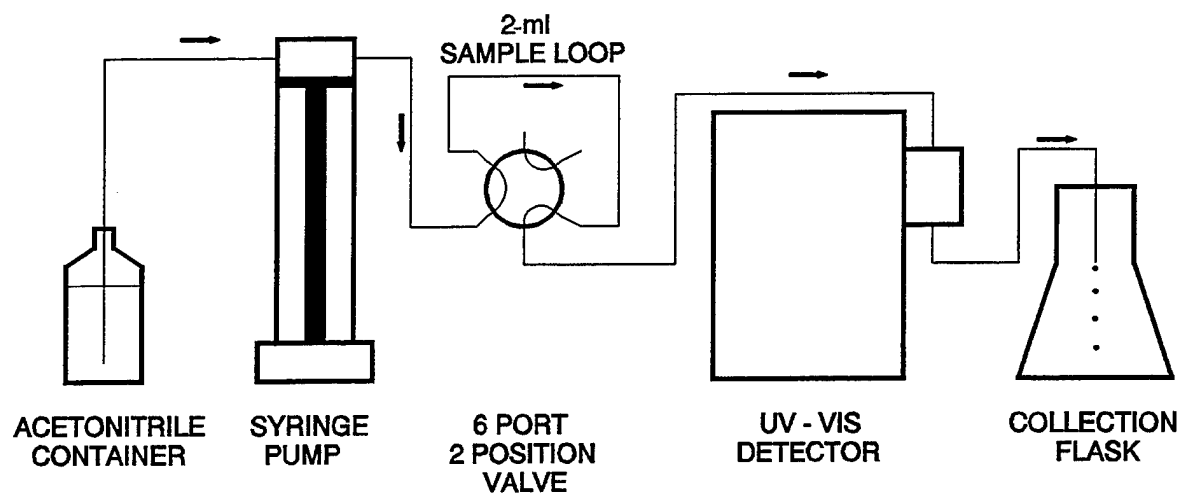


Figure 3. Apparatus for calibration of the UV-Vis detector.

absorption peak shape, width, and maximum in the range of 220–300 nm. The lack of significant variations in peak shape and position over the temperature and pressure range of these seven spectra indicate that RDX is probably not subject to the type of density-dependent changes in molar absorptivity that have been reported for anthracene and pyrene solutes in CO₂ [33]. The seven spectra taken in supercritical CO₂ were averaged for comparison with the spectra taken in acetonitrile. The averaged spectra of RDX in acetonitrile and RDX in supercritical CO₂ are shown in Figure 4. These averaged spectra are normalized to the peak maximum of the lowest energy UV transition that occurs in the range of 220–300 nm.

In order to use the acetonitrile calibration standards to determine the concentration of RDX in the 250-nl detector volume, the two averaged spectra for RDX dissolved in acetonitrile and RDX dissolved in supercritical CO₂ need to be superimposable in the wavelength region where the UV absorption measurements are made, using only a linear shift of the wavelength scale. A good empirical match is observed between the averaged spectra of RDX in supercritical CO₂ and an 8-nm blueshift of the averaged spectra of RDX in acetonitrile in the range of 220–300 nm. The UV absorbance data for RDX in CO₂, which was collected at 246 nm, was calibrated using the RDX standards in acetonitrile at 254 nm. A Beer's Law plot of the absorbance at 254 nm of RDX in acetonitrile was found to be linear over the entire range of standards.

A typical RDX solubility profile in CO₂ is shown in Figure 5. A UV absorbance baseline was established by collecting data with the extraction vessel offline, allowing RDX-free CO₂ to flow through the detector. After 10 min, the extraction vessel was put online, allowing CO₂ to flow through it and saturate with RDX.

Equilibration typically occurred within several min after placing the extraction vessel online. The variable restrictor was adjusted to keep the flow rate of liquid CO₂ measured at the pump around 0.5 ml/min or less. The actual flow of supercritical CO₂ was somewhat higher, as determined by the ratio of CO₂ density in the liquid and supercritical states at the same pressure but

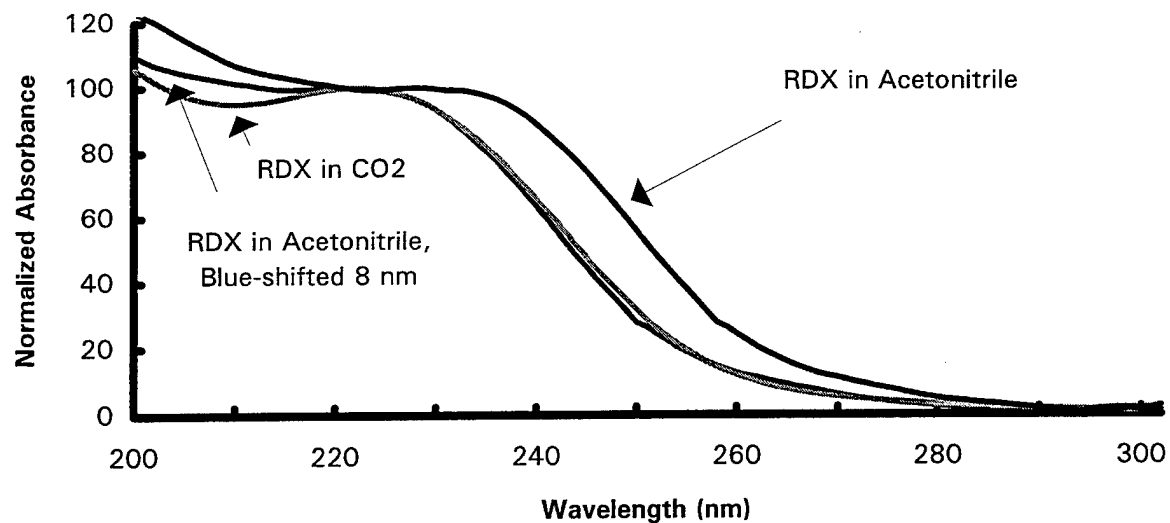


Figure 4. Spectral shift of RDX in CO₂ relative to RDX in acetonitrile calibration solutions.

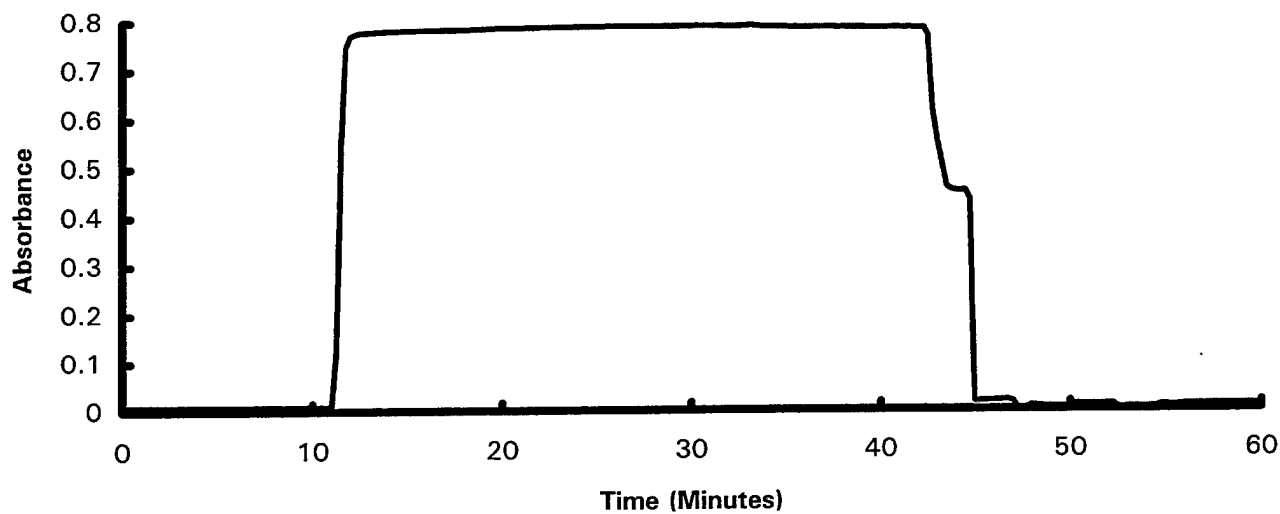


Figure 5. Typical RDX solubility profile in CO₂ at 246 nm. The extraction vessel was put online at 10 min.

different temperatures. Equilibration of the solubility measurement was checked at 323 K and 41.4 MPa by repeating the solubility measurement at different CO₂ flow rates. The solubility measurement was found to be independent of flow rate over the range of 0.2 ml/min to 1.8 ml/min at 323 K and 41.4 MPa, indicating that the SF was saturated with solute. If the fluid was not saturated with solute at the higher flow rates, an increase in solute concentration would have been observed at lower flow rates, due to the longer residence time of the fluid through the extraction vessel.

The net RDX absorbance for each run was determined by subtracting the average baseline level from the average RDX level after the system equilibrated. This absorbance measurement was converted into an RDX concentration per volume (milligrams RDX/milliliter fluid) by using the detector calibration determined with the acetonitrile standards at 254 nm. The CO₂ density in the detector flow cell was then used to determine the RDX concentration per mass CO₂ (milligrams RDX/gram CO₂), which was subsequently converted into an RDX solubility mole fraction. This technique of flowing CO₂ through a vessel filled with solute and determining the mass of sample dissolved is an example of a dynamic solubility determination [34].

3. RESULTS AND DISCUSSION

3.1 RDX Solubility in CO₂. Measurements of the solubility of RDX in CO₂ were made at the temperatures and pressures indicated in Table 1. It should be pointed out that CO₂ is not supercritical at 303 K or 6.9 MPa. Unless otherwise indicated in Table 1, only a single measurement was made at each set of temperature and pressure conditions. The only set of conditions from which enough solubility measurements were made to get a meaningful error estimate (1 standard deviation) was at 323 K and 41.4 MPa. Under these conditions, the solubility was determined to be 0.097 ± 0.009 mg RDX per gram CO₂.

Table 1. Solubility of RDX in CO₂ (Milligrams RDX/Gram CO₂) as a Function of Temperature and Pressure

MPa	303 K	308 K	323 K	338 K	353 K
6.9	0.002	0.000	0.000	—	—
10.4	0.007	0.008	0.003	0.001	—
13.8	0.013	0.013	0.013	0.009	0.004
27.6	0.032	0.034	0.051	0.076	0.114
41.4	0.053	0.067	0.097 ^a	0.173	0.237 ^b
48.3	0.055	0.064	0.111	0.173	0.254 ^b

^a Average of seven measurements. Error estimate: 0.009 mg RDX/g CO₂.

^b Average of two measurements.

Bartle et al. [35] outline a fit of solubility data to the following equations:

$$\ln(E) = a + b \cdot \rho \quad (1)$$

$$E = x \cdot P / P_{\text{vap}}, \quad (2)$$

where the constants “a” and “b” are fitting parameters, “ ρ ” is the system density, “x” is the solute (RDX) mole fraction, “P” is the system pressure, and “ P_{vap} ” is the solute vapor pressure. The quantity “E,” defined in equation 2, represents the enhancement of solute concentration in the supercritical phase relative to the concentration based upon its vapor pressure. For dilute solutions, the density of CO₂ can be used to approximate ρ . Since P_{vap} and ρ are both temperature-dependent quantities, equations 1 and 2 are used to make isothermal fits to the solubility data. The fitting parameters can be obtained by calculating E for each condition of temperature and pressure and performing a linear regression on equation 1. The RDX mole fraction data are calculated from the solubility values listed in Table 1. The RDX vapor pressure data of Dionne et al. [36] used to make these fits are listed in Table 2. CO₂ density values were obtained using the ISCO computer program SF-Solver [37]. Figure 6 shows a plot of these calculated CO₂ density values as a function of

temperature and pressure. The resulting fitting parameters are listed in Table 2. Equations 1 and 2 can be rewritten as:

$$x = (P_{\text{vap}}/P) \exp(a + b \cdot \rho). \quad (3)$$

Figure 7 shows the fit of equation 3 to the RDX mole fraction data in CO₂.

Table 2. RDX Vapor Pressure^a (P_{vap}) and Fitting Parameters for RDX Solubility in CO₂

	303 K	308 K	323 K	338 K	353 K
P_{vap} (MPa)	1.42×10^{-12}	3.16×10^{-12}	2.98×10^{-11}	2.31×10^{-10}	1.50×10^{-9}
a	3.976	4.509	6.003	6.705	4.701
b (m ³ /kg)	0.01545	0.01452	0.01163	0.00994	0.01122

^a See Dionne et al. [36].

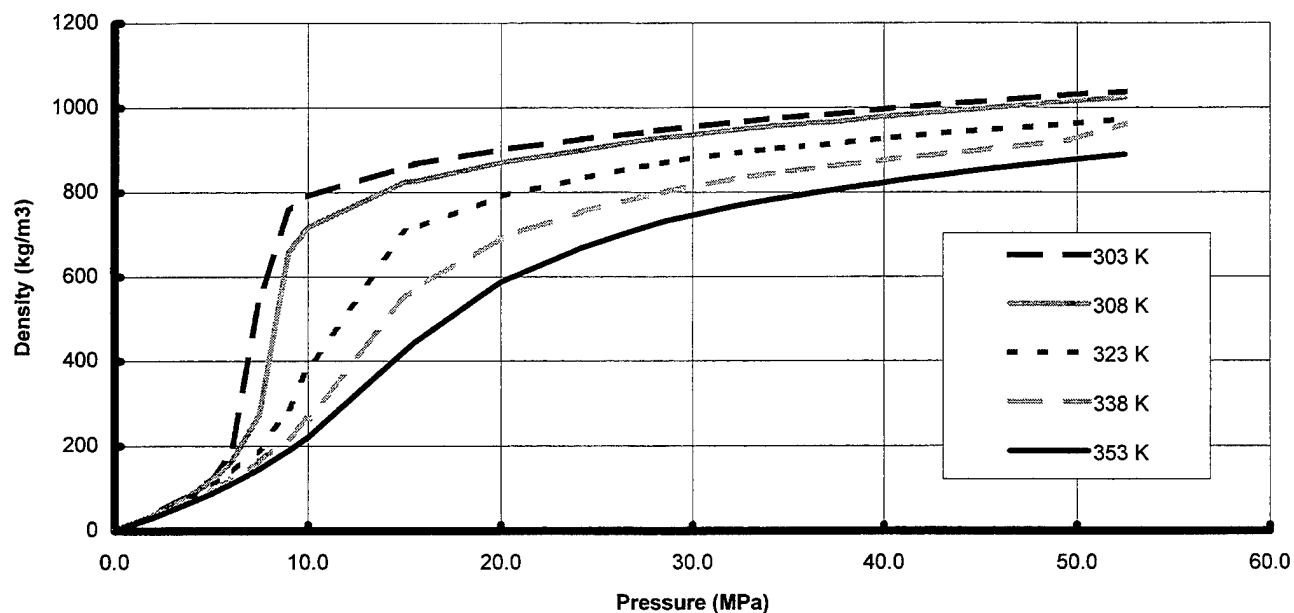


Figure 6. Density of CO₂ as a function of temperature and pressure.

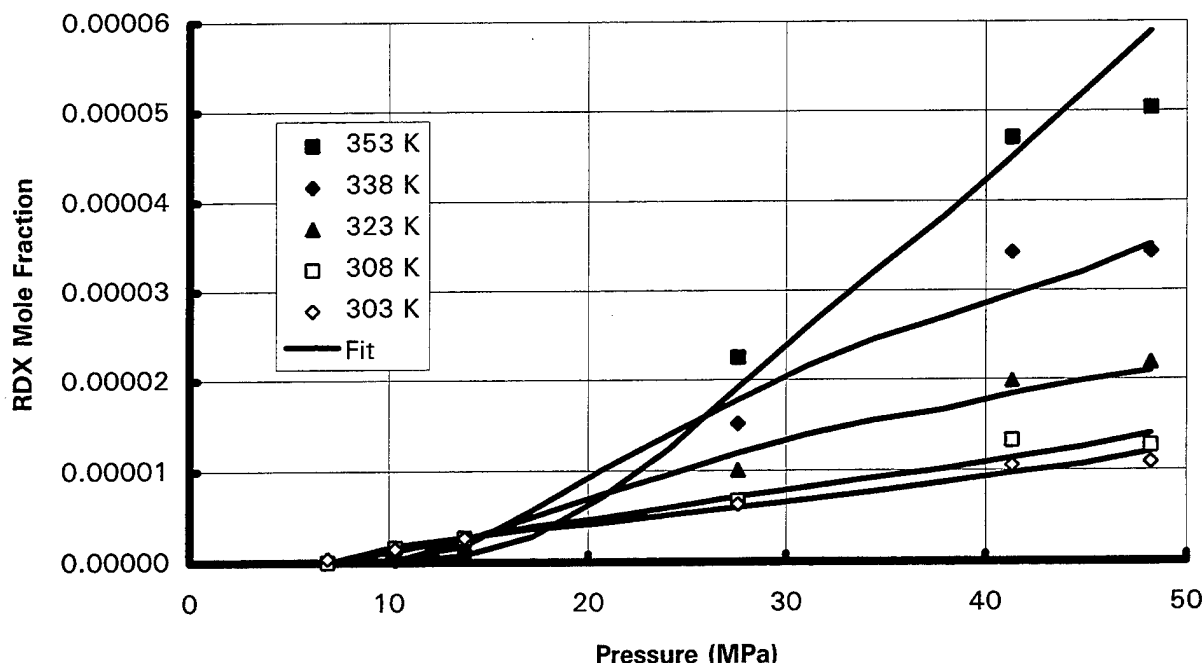


Figure 7. RDX mole fraction in CO₂ as a function of temperature and pressure.

The form of the solubility isotherms shown in Figure 7 is typical of most materials. Solubility isotherms for almost 90 low-volatility substances can be found in Bartle et al. [35]. The crossing of the RDX solubility isotherms that occurs in the pressure range of 10–20 MPa is due to competition between two physicochemical properties. Most organic compounds show an increase in solubility in CO₂ at higher pressures and temperatures. From equation 3, it should be clear that the temperature dependence of the solubility is functionally related to the solute vapor pressure and the fluid density. Raising the temperature results in an increase in the RDX vapor pressure (see Table 2) and a decrease in the CO₂ density (see Figure 6). Also, the vapor pressure occurs as a linear term in equation 3, while the density occurs within an exponential term. At lower pressures, the effect due to the decrease in CO₂ density as the temperature is raised is greater than that due to the increase in solute vapor pressure, resulting in lower solubilities. When the pressure is raised high enough, the decrease in CO₂ density with increasing temperature is less than that observed at lower pressures, and raising the temperature results in an increase in solubility, as can be seen in the highest pressure region in Figure 7.

3.2 TNT Solubility in CO₂. The solubility of TNT in CO₂ was also investigated at the ARL. Measurements were made using the experimental setup shown in Figure 2, with the exception that the UV-Vis detector was not used. TNT was found to be so soluble in CO₂ that the UV absorbance of the solution exhibited severe nonlinear deviations from Beer's Law due to the high TNT concentration. As an alternative means to determine the mass of TNT dissolved in the CO₂, following each run the acetonitrile solution in the collection flask was analyzed via high-performance liquid chromatography (HPLC) using UV detection at 246 nm. These TNT solubility data are presented in Table 3. Error estimates (one standard deviation) for the measurements made at 293 K are presented in the footnotes to Table 3. These error estimates are substantially larger, on a percentage basis, than those for the online UV-Vis determination of RDX. The main reason for the increase in the uncertainty of the HPLC method is that it is possible to form acetonitrile aerosols as the CO₂ is depressurized in the collection flask. Some of the solute can be trapped and lost in these aerosols.

Table 3. Solubility of TNT in CO₂ (Milligrams TNT/Gram CO₂) as a Function of Temperature and Pressure

MPa	293 K	308 K
13.8	4.9 ^a	9.6
37.9	13.3 ^b	—

^a Average of five measurements. Error estimate: 2.5 mg TNT/g CO₂.

^b Average of five measurements. Error estimate: 5.0 mg TNT/g CO₂.

Shortly after these TNT solubility measurements were begun, an extensive set of data on the solubility of TNT in CO₂ was published by a group of researchers at ICT [32]. The ICT solubility measurements covered a pressure range of 15 to 50 MPa and a temperature range of 303 to 413 K. At the highest combinations of temperature and pressure, the ICT data indicated TNT solubilities in excess of 55 mg/g CO₂. It should be noted that the data in Table 3 are consistent with those published by ICT.

3.3 Comparison of RDX and TNT Solubilities in CO₂. The RDX and TNT solubility data presented in Table 1, Table 3, and in Teipel, Gerber, and Krause [32] can be used to determine the relative solubility of RDX and TNT in CO₂ as a function of temperature and pressure. Ratios of TNT solubility to RDX solubility, representing the relative potential for CO₂ to selectively extract TNT in the presence of RDX, are presented as a function of temperature and pressure in Table 4.

Table 4. Solubility Ratios of TNT Relative to RDX in CO₂ as a Function of Temperature and Pressure

MPa	303 K	308 K	323 K	338 K	353 K
13.8	—	740	—	—	—
27.6	560	540	380	260	170
41.4	610	520	470	>320	>230
48.3	720	790	>490	>320	>220

TNT was found to be at least 2 orders of magnitude more soluble in CO₂ than RDX for the range of temperatures and pressures reported in Table 4. The relative solubilities of TNT and RDX can be explained by considering two physicochemical properties of these solutes: permanent dipole moment and vapor pressure. Molecular mass is not a consideration since RDX (M = 222) and TNT (M = 227) have nearly identical masses. The dipole moments for RDX [38] and TNT [39] have been determined through ab initio Hartree-Fock self-consistent field calculations to be 1.5 debye for TNT and 6.5 debye for RDX. Keeping in mind the heuristic “like dissolves like,” one can see why the less polar TNT molecule would have a greater solubility in CO₂ (permanent dipole moment = 0) than does the highly polar RDX molecule. The fact that either of these molecules is even sparingly soluble in CO₂ can be attributed to the relatively large quadrupole moment of CO₂ that results from its π bonding structure, and the $1/r^8$ dipole-quadrupole potential energy interaction [40].

Vapor pressure data for TNT and RDX are available in Dionne et al. [36], and are plotted in Figure 8. TNT has a vapor pressure at least 2 orders of magnitude greater than that of RDX over a range of temperatures from 303 to 353 K. The fact that the relative vapor pressures of TNT and RDX track their relative solubilities in CO_2 comes as no great surprise when one considers the functional dependence of the enhancement factor, E , upon vapor pressure in equation 3, although one should bear in mind that the contributions of the fitting parameters "a" and "b" have not been fully considered.

The ability to selectively remove TNT in the presence of RDX was demonstrated on a 50:50 (by mass) mixture of the two explosives. The mixture was prepared by placing powder samples of TNT and RDX in a vial and shaking the vial. The equipment shown in Figure 2 was used, without the UV-Vis detector, to extract the TNT from the mixture. A 292-mg sample of the RDX/TNT mixture was placed in a 7.5-ml extraction vessel and installed in the extraction unit. The extraction was carried out at 323 K and 13.8 MPa using a large excess—210 g—of CO_2 . The temperature and pressure for this demonstration were selected arbitrarily, since TNT will be at least 2 orders of magnitude more soluble than RDX over a large range of pressures and temperatures (see Table 4). The mass of CO_2 used represents the entire capacity of the syringe pump. An extraction demonstration using inert materials is best done by packing the materials into an extraction vessel to avoid solvent channeling through the vessel. Given the hazardous nature of TNT and RDX, it is preferable to leave a large amount of dead volume in the vessel. Since the use of an unpacked vessel is not an optimum arrangement from an extraction point of view, the entire volume of the pump was discharged through the extraction vessel to ensure complete removal of TNT from the sample.

HPLC was used to compare the composition of the mixture before extraction to that of the material remaining behind in the extraction vessel following extraction. The resulting chromatograms are shown in Figure 9. The material remaining behind was found to contain less than 1% TNT. Analysis of the recovered TNT revealed that about 2 mg of RDX were also extracted. The quantity of RDX extracted was consistent with the solubility values in Table 1 for the amount of CO_2 used.

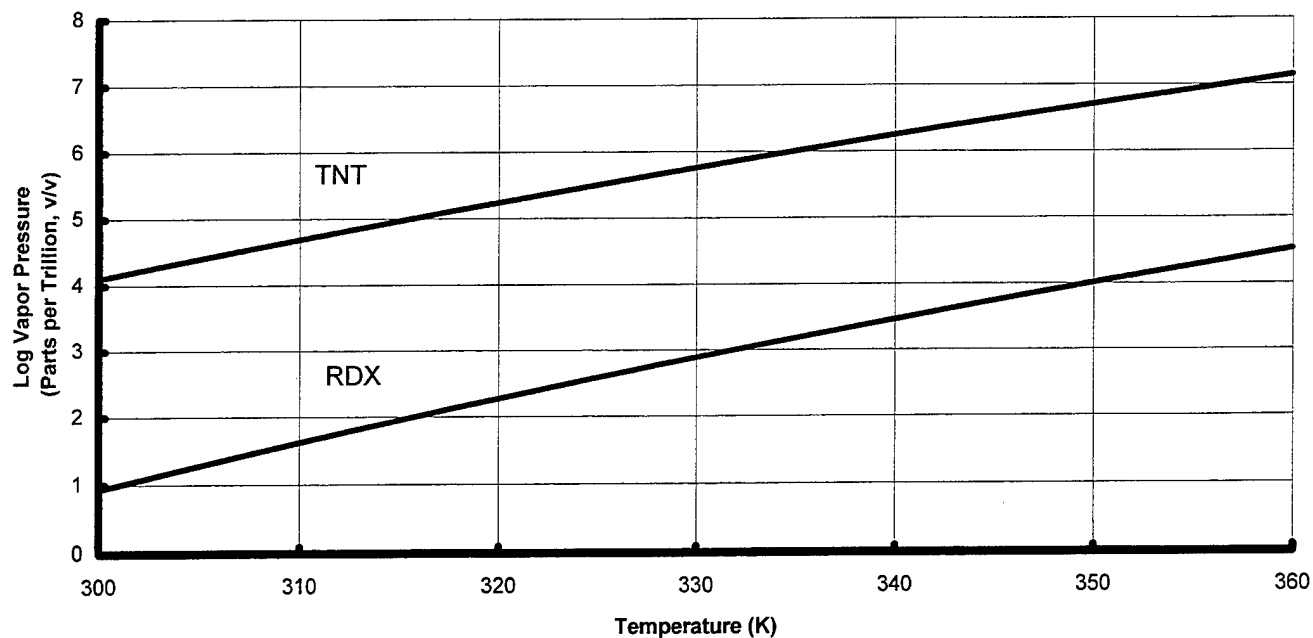


Figure 8. Vapor pressures of RDX and TNT, plotted as $\log(P_{\text{vap}})$ vs. temperature.

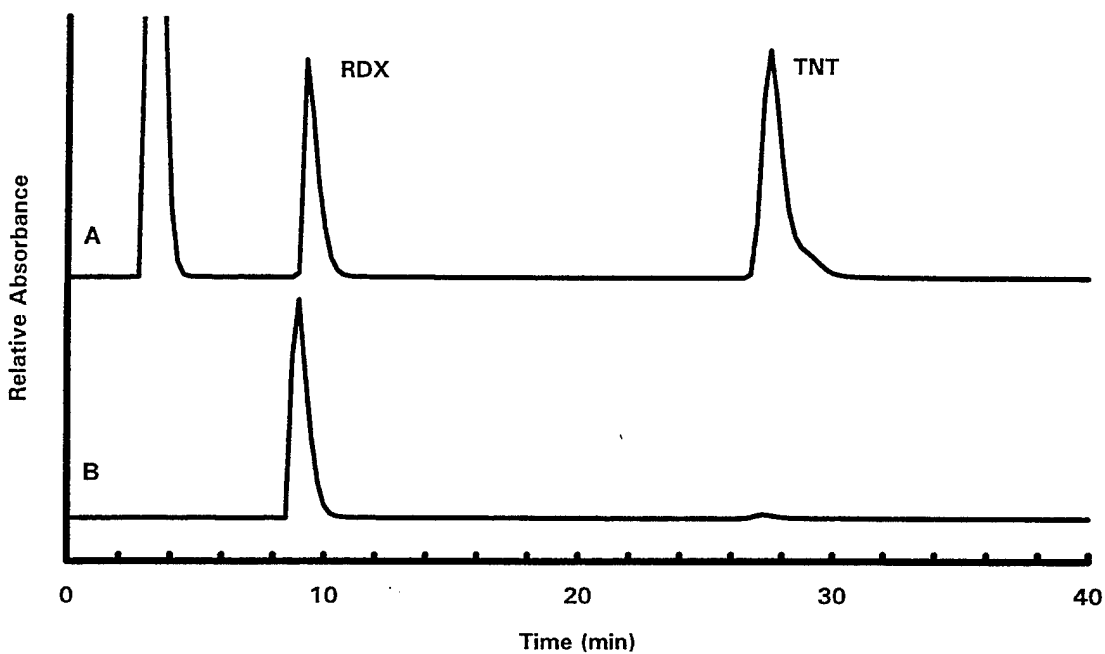


Figure 9. Separation of a mixture of RDX and TNT powders using CO_2 at 323 K and 13.8 MPa: Chromatograms using 246-nm detection of (A) unextracted mixture and (B) recovered material following extraction. The unidentified peak in (A) is due to acetone used to dissolve the sample; acetonitrile was used to dissolve the recovered material in (B).

4. CONCLUSIONS

This report discusses solubility measurements of RDX and TNT in liquid and supercritical CO₂. While RDX was already known to display limited solubility in CO₂, its solubility was found to vary by over 2 orders of magnitude, depending on the solvent temperature and pressure. It was possible to fit the logarithm of the RDX solubility to a linear function of solvent density under isothermal conditions.

Recently published solubility data for TNT was compared with that of RDX. TNT was found to be 2–3 orders of magnitude more soluble than RDX in supercritical CO₂ over a wide range of temperatures and pressures.

The large differences in solubility in CO₂ displayed by RDX and TNT were used to demonstrate the potential for selective separation of these explosive components. TNT was selectively extracted from a mixture of RDX and TNT powders. Future efforts along these lines will be directed towards the separation of RDX from TNT in formulations such as Composition B.

INTENTIONALLY LEFT BLANK.

5. REFERENCES

1. Matson, D. W., B. W. Wright, R. D. Smith, W. S. Melvin, and J. F. Graham. "Applications of Supercritical Fluid Systems to Solid Rocket Propellants." Proceedings of the 1987 JANNAF Propulsion Meeting, CPIA Pub. 480, vol. 3, pp. 401-408, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, December 1987.
2. Melvin, W. S. "Extraction and Recovery of Plasticizers From Solid Propellants and Munitions." U.S. Patent 4,909,868, 20 March 1990.
3. Ashraf-Khorassani, M., and L. T. Taylor. "Coupled Supercritical Fluid Chromatography and Supercritical Fluid Extraction of Nonpolymeric Ingredients in Double-Base Propellants." Proceedings of the 1988 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. 497, pp. 105-112, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, November 1988.
4. Ashraf-Khorassani, M., and L. T. Taylor. "Qualitative Supercritical Fluid Chromatography/Fourier Transform Infrared Spectroscopy Study of Methylene Chloride and Supercritical Carbon Dioxide Extracts of Double-Base Propellant." Analytical Chemistry, vol. 61, pp. 145-148, 1989.
5. Via, J., and L. T. Taylor. "Chromatographic Behavior of N-Nitrosodiphenylamine and Diphenylamine." Proceedings of the 1990 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 545, pp. 225-234, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, November 1990.
6. Via, J. C., and L. T. Taylor. "Chromatographic Analysis of Nonpolymeric Single-Base Propellant Components." Journal of Chromatographic Science, vol. 30, pp. 106-110, March 1992.
7. Taylor, L. "The Supercritical Fluid Extraction and Analysis of Aged Single-Base Propellants." American Laboratory, pp. 22-26, May 1993.
8. Naufflett, G. W., and R. E. Farncomb. "Processing of Energetic Materials With Supercritical Fluids." Proceedings of the 1992 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 588, pp. 417-435, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, August 1992.
9. Farncomb, R. E., and G. W. Naufflett. "Removal of Lead and Copper from a Double-Base Propellant." Proceedings of the 1993 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 600, pp. 297-304, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, August 1993.

10. Farncomb, R. E., and G. W. Naufflett. "Supercritical Fluid Extraction of Depleted Stabilizers From Single-Base Propellant and Adding New Stabilizers." Proceedings of the 1993 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 600, pp. 305-309, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, August 1993.
11. Thomas, B. P. "Quantitative Extraction of Gun Propellant Using Supercritical Carbon Dioxide." Proceedings of the 1992 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 578, pp. 149-158, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, April 1992.
12. Krukonis, V. J., M. P. Coffey, and P. M. Gallagher. "Exploratory Development on a New Process to Produce Improved RDX Crystals: Supercritical Fluid Antisolvent Recrystallization." BRL-CR-606, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, January 1989.
13. Gallagher, P. M., M. P. Coffey, V. J. Krukonis, and N. Klasutis. "Gas Antisolvent Recrystallization: New Process to Recrystallize Compounds Insoluble in Supercritical Fluids." Supercritical Fluid Science and Technology. Edited by K. P. Johnston and J. M. L. Penninger. ACS Symposium Series No. 406, pp. 334-354, American Chemical Society, Washington D.C., 1989.
14. Farncomb, R. E., and G. W. Naufflett. "Supercritical Fluid Carbon Dioxide Crystallization of Energetic Materials." Proceedings of the 1995 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 625, pp. 467-474, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, April 1995.
15. Morris, J. B., R. A. Fifer, K. L. McNesby, R. A. Pesce-Rodriguez, and M. A. Schroeder. "Supercritical Fluids: An Alternative to the Use of Organic Solvents for Extraction of Energetic Materials From Solid Gun Propellants." Proceedings of the 1993 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 597, pp. 357-362, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, April 1993.
16. Morris, J. B., K. L. McNesby, M. A. Schroeder, R. A. Pesce-Rodriguez, and R. A. Fifer. "Analytical and Bench Scale Supercritical Fluid Extraction Studies of Nitramine-Based Gun Propellant." Proceedings of the 1994 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 614, vol. 1, pp. 361-370, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, August 1994.

17. Morris, J. B., M. A. Schroeder, R. A. Pesce-Rodriguez, K. L. McNesby, and R. A. Fifer. "Supercritical Fluid Extraction of Nitramine-Based Munitions Using Modified Carbon Dioxide: A Study of Modifier Chemical and Physical Relationships." Proceedings of the 1995 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 625, pp. 229-238, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, April 1995.
18. Morris, J. B., M. A. Schroeder, R. A. Pesce-Rodriguez, K. L. McNesby, and R. A. Fifer. "Supercritical Fluid Extraction of Nitramine-Based Gun Propellant: A Fluid Survey." ARL-TR-885, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, October 1995.
19. Ashraf-Khorassani, M., and L. T. Taylor. "Analysis of Crude, Purified, and Synthetic Candelilla Wax Employing Supercritical Fluids." Proceedings of the 1989 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 527, pp. 157-164, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, November 1989.
20. Burrows, R., R. J. Laub, and D. Song. "Some Fundamental Aspects of Speciation of Propellant Binder Prepolymers. VI. Application of Inverse Gas Chromatography to Lots of Bulk Hydroxy-Terminated Polybutadiene." Proceedings of the 1989 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 527, pp. 271-284, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, November 1989.
21. Watkins, J. J., and V. J. Krukoni. "Supercritical Fluid Processing of Propellant Binders: A. Fractionation of Hydroxy-Terminated Polybutadiene, B. Extraction of Nonfunctional Cyclics from Glycidyl Azide Polymer (GAP)." Proceedings of the 1990 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 545, pp. 313-322, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, November 1990.
22. DiNoia, T. P., and M. A. McHugh. Solubility and Phase Behavior of PEP Binders in Supercritical Carbon Dioxide. CPIA Pub. 646, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, November 1996.
23. McHugh, M. A., and V. J. Krukoni. Supercritical Fluid Extraction. Second Edition, p. 14. Boston: Butterworth-Heinemann, 1994.
24. Chester, T. L., J. D. Pinkerton, and D. E. Raynie. "Supercritical Fluid Chromatography and Extraction." Analytical Chemistry, vol. 68, pp. 487R-514R, 1996.
25. Melvin, W. S. "Critical Fluid Demilitarization and Ingredient Reclamation Technology." Proceedings of the 1992 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 588, pp. 297-312, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, August 1992.

26. Reader, G. E., D. H. Mitchell, K. K. Light, M. E. Morgan, P. G. Schirk, O. J. Manar, W. S. Melvin, and N. W. Rizzardi. "Process Development for Rocket Motor Demilitarization and Ingredient Recovery Using Ammonia." Proceedings of the 1993 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 600, pp. 381–392, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, August 1993.
27. Melvin, W. S., and J. S. Wright. "Recovery and Reuse of Rocket Motor Propellant Ingredients." Proceedings of the 1994 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 614, vol. 1, pp. 427–435, Johns Hopkins University Chemical Propulsion Information Agency, Columbia, MD, August 1994.
28. Melvin, W. S., and J. F. Graham. "Method to Demilitarize, Extract, and Recover Ammonium Perchlorate From Composite Propellants Using Liquid Ammonia." U.S. Patent 4,854,982, 8 August 1993.
29. Melvin, W. S. "Method to Extract and Recover Nitramine Oxidizers From Solid Propellants Using Liquid Ammonia." U.S. Patent 5,284,995, 8 February 1994.
30. Braker, W., and A. L. Mossman. Matheson Gas Data Book. Sixth edition, pp. 120–129, Lyndhurst, NJ: Matheson, 1980.
31. McHugh, M. A., and V. J. Krukonsis. Supercritical Fluid Extraction. Second edition, Boston: Butterworth-Heinemann, 1994.
32. Teipel, U., P. Gerber, and H. Krause. "Characterization of the Phase Equilibrium of the System Trinitrotoluene-Carbon Dioxide." Energetic Materials - Technology, Manufacturing and Processing, Proceedings of the the 27th International Annual Conference of ICT, Fraunhofer Institut für Chemische Technologie, Karlsruhe, Germany, pp. 127-1–127-11, June 1996.
33. Rice, J. K., E. D. Niemeyer, and F. V. Bright. "Evidence for Density-Dependent Changes in Solute Molar Absorptivities in Supercritical CO₂: Impact on Solubility Determination Practices." Analytical Chemistry, vol. 67, pp. 4354–4357, December 1995.
34. McHugh, M. A., and V. J. Krukonsis. Supercritical Fluid Extraction. Second edition, pp. 85–94, Boston: Butterworth-Heinemann, 1994.
35. Bartle, K. D., A. A. Clifford, S. A. Jafar, and G. F. Shilstone. "Solubilities of Solids and Liquids of Low Volatility." Journal of Physical and Chemical Reference Data, vol. 20, pp. 713–756, 1991.
36. Dionne, B. C., D. P. Rounbehler, E. K. Achter, J. R. Hobbs, and D. H. Fine. "Vapor Pressure of Explosives." Journal of Energetic Materials, vol. 4, pp. 447–472, 1986.

37. SF-Solver software for IBM-PC, Ver. 2.5.1. Lincoln, NE: ISCO, Inc., 1991.
38. Zahner, P. Solvation of RDX as a Function of the Dielectric Constant of the Solvent. Master of Science Thesis, Oklahoma State University, Stillwater, OK, 1995.
39. Rice, B. M., and C. F. Chabalowski. Unpublished results, U. S. Army Research Laboratory, Aberdeen Proving Ground, MD, 1995.
40. McHugh, M. A., and V. J. Krukoni. Supercritical Fluid Extraction. Second edition, pp. 99–101, Boston: Butterworth-Heinemann, 1994.

INTENTIONALLY LEFT BLANK.

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
2	DEFENSE TECHNICAL INFO CTR ATTN DTIC DDA 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	HQDA DAMO FDQ ATTN DENNIS SCHMIDT 400 ARMY PENTAGON WASHINGTON DC 20310-0460
1	US MILITARY ACADEMY MATH SCI CTR OF EXCELLENCE DEPT OF MATHEMATICAL SCI ATTN MDN A MAJ DON ENGEN THAYER HALL WEST POINT NY 10996-1786
1	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL CS AL TP 2800 POWDER MILL RD ADELPHI MD 20783-1145
1	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL CS AL TA 2800 POWDER MILL RD ADELPHI MD 20783-1145
3	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL CI LL 2800 POWDER MILL RD ADELPHI MD 20783-1145
	<u>ABERDEEN PROVING GROUND</u>
2	DIR USARL ATTN AMSRL CI LP (305)

NO. OF
COPIES ORGANIZATION

1 CDR ARDEC
ATTN AMSTA AR ET J BORRI
PCTNY ARSNL NJ 07806-5000

1 CDR ARDEC
ATTN AMSTA AR AES R GOLDSTEIN
PCTNY ARSNL NJ 07806-5000

1 CDR ARDEC
ATTN AMSMC PBE R GOLDBERG
PCTNY ARSNL NJ 07806-5000

2 CDR MRDEC
ATTN AMSMI RD PR T
J CARVER
R W MELVIN
REDSTONE ARSNL AL 35898-5249

1 CMDT
USA DEFNS AMMO CTR & SCHOOL
ATTN SIOAC TDM E ANSELL
SAVANNA IL 61074-9639

1 OFFICE OF NAVAL RESEARCH
ATTN R MILLER
ONR 333 800 N QUINCY STR
ARLINGTON VA 22217-5660

1 NAWC
ATTN P CARPENTER
CODE 473430D
CHINA LAKE CA 93555

2 NSWC
ATTN G NAUFLETT
CODE 1930G
R FARNCOMB CODE 1930I
INDIAN HEAD MD 20640-5035

1 WRIGHT LABORATORY
ATTN MLSE P MYKYTIUK
BUILDING 652
2179 TWELFTH STREET STE 1
WRIGHT-PATTERSON AFB, OH
45433-7718

1 DIR LANL
ATTN P DELLORCO MS C920
LOS ALAMOS NM 87545

NO. OF
COPIES ORGANIZATION

1 DIR SNL
ATTN E RUSSICK DEPT 1815
MS 0367
PO BOX 5800
ALBUQUERQUE NM 87185-0367

1 JHU/CPIA
ATTN J COCCHIARO
10630 LITTLE PATUXENT PKWY
STE 202
COLUMBIA, MD 21044-3200

1 JHU
DEPT OF CHEMICAL ENGRG
ATTN M MCHUGH
BALTIMORE MD 21218

1 VA POLYTECH INST & ST UNIV
DEPT OF CHEMISTRY
ATTN L TAYLOR
BLACKSBURG VA 24061-0212

1 APPLITECH CORP
ATTN J WRIGHT
PO BOX 265
NOTTINGHAM PA 19362

1 BATTELLE PANTEX
ATTN C CLICK
PO BOX 30020
AMARILLO TX 79177

1 CONCURRENT TECH CORP
ATTN A QAZI
1450 SCALP AVE
JOHNSTOWN PA 15904

1 HOLSTON DEFENSE CORP
ATTN M SMITH
4509 WEST STONE DR
PO BOX 1483
KINGSPORT TN 37662-1483

1 LABAT ANDERSON INC
SERDP SUPPORT OFC
ATTN B HENKE
8000 WESTPARK DR STE 400
MCLEAN VA 22102

NO. OF
COPIES ORGANIZATION

1 MASON & HANGER
SILAS MASON CO
INC
ATTN B RICHARDSON
PO BOX 30020
PANTEX PLANT
AMARILLO TX 79177

1 OLIN ORDNANCE
ATTN A CALABRESE
PO BOX 222
ST MARKS FL 32355-0222

1 OLIN ORDNANCE
ATTN H MCELROY
10101 NINTH ST NORTH
ST PETERSBURG FL 33716

1 PHASEX CORP
ATTN V KRUKONIS
360 MERRIMACK ST
LAWRENCE MA 01843

1 POLYMER SOLUTIONS INC
ATTN J RANCOURT
1872 PRATT DR
BLACKSBURG VA 24060

1 SUPERCRITICAL FLUID TECH INC
ATTN KEN JAMES
PO BOX 4548
NEWARK DE 19715-4548

ABERDEEN PROVING GROUND

2 CDR USAATC
ATTN STEAC-TS-PC, P. MARSH (B363)
STEAC-TS-PC, A. RAUNIG (B363)

49 DIR USARL
ATTN AMSRL-WM-TB,
R. FREY
W. HILLSTROM (2 CP)

NO. OF
COPIES ORGANIZATION

AMSRL-WM-P,
A.W. HORST
AMSRL-WM-PC,
B.E. FORCH
G.F. ADAMS
W.R. ANDERSON
R.A. BEYER
S.W. BUNTE
C.F. CHABALOWSKI
K.P. MCNEILL-
BOONSTOPPEL
A. COHEN
R. CUMPTON
R. DANIEL
D. DEVYNCK
R.A. FIFER
J.M. HEIMERL
B.E. HOMAN
A. JUHASZ
A.J. KOTLAR
R. KRANZE
E. LANCASTER
W.F. MCBRATNEY
K.L. MCNESBY
M. MCQUAID
N.E. MEAGHER
M.S. MILLER
A.W. MIZIOLEK
J.B. MORRIS (6 CP)
J.E. NEWBERRY
S.V. PAI
R.A. PESCE-RODRIGUEZ
J. RASIMAS
P. REEVES
B.M. RICE
P. SAEGAR
R.C. SAUSA
M.A. SCHROEDER
R. SCHWEITZER
L.D. SEGER
J.A. VANDERHOFF
D. VENIZELOS
A. WHREN
H.L. WILLIAMS

INTENTIONALLY LEFT BLANK.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project(0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 1997		3. REPORT TYPE AND DATES COVERED Final, Sep 95 - Mar 96
4. TITLE AND SUBTITLE Relative Solubility of RDX and TNT in Supercritical CO ₂			5. FUNDING NUMBERS PR: 1L161102AH43	
6. AUTHOR(S) Jeffery B. Morris				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Director U.S. Army Research Laboratory ATTN: AMSRL-WM-PC Aberdeen Proving Ground, MD 21005-5066			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-1343	
9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES This work was supported by the Strategic Environmental Research and Development Program, Project PP-660.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>Mixtures of 2,4,6-trinitrotoluene (TNT) and the nitramines cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) are used in a variety of high-explosive formulations, such as Composition B (RDX/TNT) or Octol (HMX/TNT). There has been much recent interest in the use of supercritical fluid (SF) CO₂ technologies for the processing and/or demilitarization of energetic materials. The solubility of RDX in neat CO₂ was measured over a temperature and pressure range of 303–353 K (30°–80° C) and 6.9–48.3 MPa (1,000–7,000 lb/in²) and is presented in this report.</p> <p>RDX was found to be relatively insoluble in neat CO₂ in the temperature and pressure range studied, with a maximum solubility of about 0.25mg/g of CO₂. Data for TNT solubility in CO₂ have recently been published by a group of researchers at the Fraunhofer Institut für Chemische Technologie. Consideration of the relative solubilities of RDX and TNT in CO₂ suggests that SF extraction (SFE) of TNT should be effective for separation and recovery of nitramine materials from TNT-based energetic formulations. RDX is found to be 2-3 orders of magnitude less soluble than TNT in SF CO₂. An SFE-based separation process is demonstrated on a synthetic mixture of RDX and TNT powders.</p>				
14. SUBJECT TERMS supercritical fluid extraction (SFE), nitramine, RDX			15. NUMBER OF PAGES 30	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

INTENTIONALLY LEFT BLANK.

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. ARL Report Number/Author ARL-TR-1343 (Morris) Date of Report April 1997
2. Date Report Received _____
3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) _____

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) _____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. _____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) _____

CURRENT
ADDRESS

Organization

Name

E-mail Name

Street or P.O. Box No.

City, State, Zip Code

7. If indicating a Change of Address or Address Correction, please provide the Current or Correct address above and the Old or Incorrect address below.

OLD
ADDRESS

Organization

Name

Street or P.O. Box No.

City, State, Zip Code

(Remove this sheet, fold as indicated, tape closed, and mail.)

(DO NOT STAPLE)

DEPARTMENT OF THE ARMY

OFFICIAL BUSINESS

BUSINESS REPLY MAIL
FIRST CLASS PERMIT NO 0001,APG,MD

POSTAGE WILL BE PAID BY ADDRESSEE

DIRECTOR
US ARMY RESEARCH LABORATORY
ATTN AMSRL WM PC
ABERDEEN PROVING GROUND MD 21005-5066



NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

